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Accepted May 27/94

Para-Methoxy-Ortho-Sulpho-
Benzoic Acid and its
Sulphon-Fluoresceins.

The Action of Absolute Methyl
Alcohol on Para-Diazo-Ortho-
Toluene-Sulphonic Acid in
the Presence of Certain Substances.

Dissertation

Submitted to the Board of
University Studies of The
Johns Hopkins University for
the Degree of Doctor of Philosophy

by
Philip Randle Moale
1894

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Acknowledgment

The work described in this paper was carried on in the chemical laboratory of the Johns Hopkins University at the suggestion and under the direct guidance of Professor Reman, to whom I am very grateful both for his valuable aid and kind interest in me. I desire also to record here my thanks to the other instructors under whom I have studied, and especially to Professors Morse and Renouf in chemistry, and Professors Williams and Clark in mineralogy and geology.

Para Methoxy-Ortho Sulpho- Benzoic Acid and its Sulphon-Fluoresceins

Introduction

The work here described is a continuation of the investigations of the derivatives of ortho-sulpho benzoic acid - a line of work which has been in progress in this laboratory for many years past.

The object in view was the study of para-methoxy-ortho-sulpho-benzoic acid, its production from para-methoxy-sulphamide and the sulphon-fluoresceins formed by it with resorcin and

rescin. Remsen and Linn¹ described the simple sulphur-fluorescein formed from ortho-sulpho-benzoin acid with resorcin. Blackshear² took up its further study and analysis. In 1880 Remsen and Fehlbeg³ first prepared ortho-sulpho benzoin acid by heating benzoin sulphimide, $\text{C}_6\text{H}_4\text{SO}_2\text{NH}$, with concentrated hydrochloric acid in a sealed tube to 150° .

Later Brackett and Hayes⁴ recommended its preparation by repeated evaporations with concentrated hydrochloric acid on the water bath. In 1887

Remsen and Hayes⁵ heated the ortho-sulpho-benzoin acid with resorcin and obtained

1 Amer. Chem. J. XI. 73

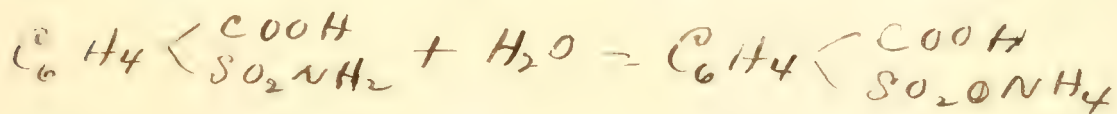
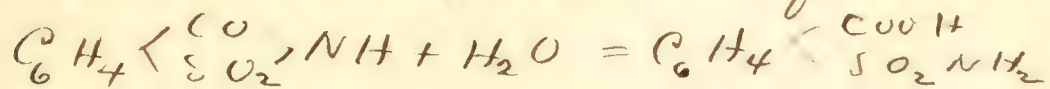
2 Amer. Chem. J. XIV. 455

3 Amer. Chem. J. I. 436

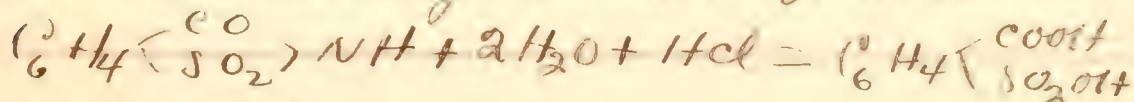
4 Amer. Chem. J. IX. 401

5 Amer. Chem. J. IX. 572

a sulphon-fluorescein, analogous to
 Baeyer's fluorescein. Remsen and
 Leon¹ repeated Brackett and Hayes'²
 work and showed that not the
 free ortho-sulpho-benzoin acid
 was formed as described, but that
 it was the acid ammonium salt
 that was produced, when the
 benzoin sulphimide was evaporated
 with concentrated hydrochloric acid.
 The reactions involved have, since,
 been shown to be the following.



whereas the reaction had previously
 been supposed to lead to the
 formation of ortho-sulphobenzoin-
 acid according to this equation.



4
I will not review here von Baeyer's
work on the phthalicins in
which investigation he first
prepared fluorescein to which
sulphon fluorescein is analogous

1 Ber d. Chem Ges 4 558 662

2 Ann Chem 183 9. 23

3 " " 202 21

Para Methoxy butic Sulpho Benzonic acid

Preparation

The preparation of the above acid involves several stages, the starting point being para toluene ortho-sulphonic acid. The directions of Parks were followed in the main, where differences occur, mention of them is made. Parks found that only the methoxy product was formed when para diags-ortho toluene sulphonic acid $\text{C}_6\text{H}_3(\text{CH}_3)(\text{SO}_3)_2$ was boiled with absolute methyl alcohol under ordinary diminished or increased pressure. As the diags compound

prepared according to the directions of Parke was at once converted into the para-methoxy-ortho-toluene sulphonic acid at ordinary pressure.

The para-methoxy-ortho-toluene-sulphonic acid was converted into the sulphon-amide through the chloride. The sulphon-amide was then oxidized with potassium permanganate to the para-methoxy-sulphinide

$$\begin{array}{c} \text{OCH}_3 \quad (4) \\ | \\ \text{C}_6\text{H}_3-\text{SO}_2\text{NH}_2 \quad (12) \\ | \\ \text{CO} \end{array}$$

As the yield of the sulphinide was very poor a few experiments to improve it were made. The quantity of water used was varied, and from three to five grams of caustic potash were added to each solution. The best

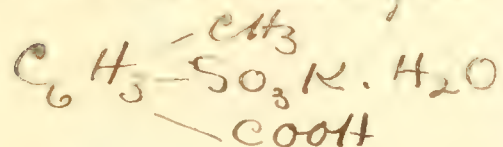
conditions were found to be as follows - to use the same amount of sulphur amide and potassium permanganate as given by Parks, and to increase the quantity of water to two liters, and to this solution add from three to five grams of potassium hydrate. The time required for the oxidation was about the same, from three to four hours. This treatment increased the yield of para-methoxy-sulphuric acid to between 25% and 30^{by}/₁₀. From the filtrate of the para-methoxy-sulphuric acid Parks first obtained potassium chloride and then the acid potassium salt of para-methoxy-ortho-sulphuric acid.

crystallized out, while it was found here by careful evaporation, the acid potassium salt first crystallized out. The acid potassium salt was identified by analysis.

I 0.1548 grams of salt lost 0.0598 gram of H_2O

II 0.2362 grams of dehydrated salt gave 0.0750 grams of K_2CO_3

Calculated for



Found

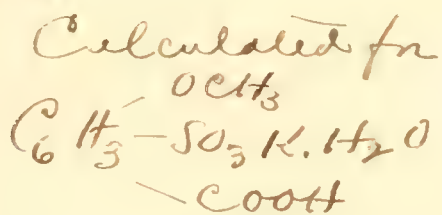
		I	II
H_2O	6.25	6.33	
K (dehydrated)	14.44		14.38

The acid potassium salt can also be made by oxidising with potassium permanganate the potassium salt of para methyl

orthotoluene-sulphonic acid. This was tried, as directed by Parks, but as the yields were not as good as through the para-methoxy-sulphinide the latter method was adopted.

The salt was identified by analysis

0.2689 grams of salt lost 2.0169 grams of H_2O and gave 0.0810 grams of K_2SO_4



Found.

H_2O 6.25 6.28

K. 13.58 13.52

Park's directions for the conversion of the para-methoxy-sulphinide and the acid potassium salt

of para-methoxy-ortho-sulph-benzoic acid into the free para-methoxy-ortho-sulph-benzoic acid were followed. The conversion of the acid potassium salt was found to be correct but the transformation of the para-methoxy-sulphinide into the acid was found to be different as will be shown further on. The following is a synopsis of the steps taken in the preparation of para-methoxy-ortho-sulph-benzoic acid.

1. $C_6H_4-CH_3$ $\begin{matrix} CH_3 \\ NO_2 (4) \end{matrix}$ by fuming H_2SO_4 to \rightarrow

2 \rightarrow $C_6H_3-CH_3$ $\begin{matrix} CH_3 \\ NO_2 (4) \\ SO_3H (2) \end{matrix}$ by reduction with Sn and HCl (conc). to \rightarrow

3 \rightarrow $C_6H_3-CH_3$ $\begin{matrix} CH_3 \\ NO_2 (4) \\ SO_3H (2) \end{matrix}$ by diazotising to \rightarrow

4 \rightarrow $C_6H_3-CH_3$ $\begin{matrix} CH_3 \\ NO_2 (4) \\ SO_3H (2) \end{matrix}$ by decomposition with absolute CH_3OH to \rightarrow

5 $C_6H_3-CH_3$ $\begin{matrix} CH_3 \\ SO_3H (2) \\ OCH_3 (4) \end{matrix}$ by oxidation with $KMnO_4$ to \rightarrow

6 \rightarrow $C_6H_3-CH_3$ $\begin{matrix} COOH \\ SO_3H (2) \\ OCH_3 (4) \end{matrix}$ by PCl_5 to \rightarrow

7 \rightarrow $C_6H_3-CH_3$ $\begin{matrix} COOH \\ SO_3H (2) \\ OCH_3 (4) \end{matrix}$ by boiling with H_2O to \rightarrow

8 \rightarrow $C_6H_3-CH_3$ $\begin{matrix} COOH \\ SO_3H (2) \\ OCH_3 (4) \end{matrix}$

(class for 3 hrs) $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_3\text{H} \cdot 2\text{H}_2\text{O}$ by PbCl_2

$\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_2\text{Cl}$ (2) by concentrated NH_4OH (4)

$\rightarrow \text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_2\text{NH}_2$ (2) by oxidation with KMnO_4 (4)

$\rightarrow \text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_2\text{Nitrated}$ $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_3\text{K}$ (4)

with H_2O and HCl

$\text{C}_6\text{H}_3(\text{CH}_3)_2\text{COOH}$ (2)
 $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_3\text{H}$ (2)
 $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OCH}_3$ (4)

by PbCl_2

$\text{C}_6\text{H}_3(\text{CH}_3)_2\text{COCl}$ (2)
 $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_2\text{Cl}$ (2)
 $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OCH}_3$ (4)

by H_2O

$\text{C}_6\text{H}_3(\text{CH}_3)_2\text{COOH}$ (2)
 $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_2\text{OH}$ (2)
 $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OCH}_3$ (4)

Conversion of Para-methoxy-benzoic sulphimide to Para-methoxy-ortho-sulpho-benzoic Acid

Having obtained the above sulphimide, Park's directions for converting it into the para-methoxy-ortho-sulphobenzoic acid were followed. The sulphimide is placed in a balloon flask, to it is added a sufficient quantity of water and hydrochloric acid, eight parts of water to one part of concentrated hydrochloric acid. The balloon flask is connected with an inverted condenser and the liquid boiled till all the para-methoxy-benzoic-sulphimide has been dissolved. The contents of the flask were then evaporated

in a beaker to crystallization. On cooling, long white needles crystallized out then was recrystallized again. Thinking this was the acid ammonium salt of para-methoxy-ortho-sulpho-benzoic acid, it was attempted to convert it into the ammonium salt of paramethoxy di-ortho-benzoyl benzene sulphonic acid $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_3(\text{SO}_3\text{ONH}_4)_2$ by treatment with urea.

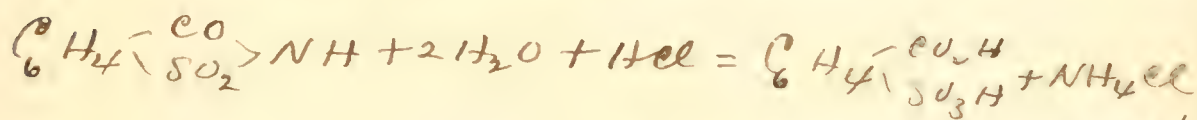
But we obtained a sulphon fluorescein. This indicated that the substance out which we started must have been the free para-methoxy-ortho-sulpho-benzoic acid itself. The same experiment was made with the same and different specimens with like results in all cases. The melting-point was taken

and the crystals melted at 104° , the melting-point of para-methoxy-ortho-sulpho-benzoic acid, thus showing that the free acid itself, instead of the acid ammonium salt, is formed by boiling para-methoxy-benzoic-sulphide with water and hydrochloric acid as directed above. Again the substance was treated with sodium hydrate and no smell of ammonia could be detected, nor its presence shown by litmus paper. This also pointed to the free acid. Other properties of the acid were tested and they agreed with Parks' description of para-methoxy-ortho-sulphobenzoic acid. It melted without decomposition at 104° and on cooling

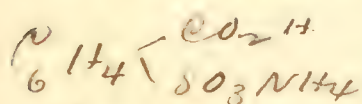
it quickly solidified and again melted at the same point when heated. Ammonium chloride was obtained and isolated as a product of the reaction. It was easily separated from the free acid by crystallization from water and alcohol. This formation of the acid direct from the sulphimide by boiling with water and hydrochloric acid is not in accordance with that described by Remsen, Linn and others, who in case of the simple benzoic sulphimide obtained the acid ammonium salt of ortho-sulpho-benzoic acid by the above mentioned method. So the formation of para-methoxy-ortho-sulpho-benzoic acid direct from the para-methoxy-benzoic-sulphimide

by boiling with water and hydrochloric acid was unexpected. The above experiments were performed repeatedly using different specimens of sulphamide and in every case the para-methoxy-ortho-sulpho-benzoic acid, melting at 174° , was obtained.

Brackett and Hayes¹ prepared ortho-sulphobenzoic acid by heating benzoic-sulphamide with concentrated hydrochloric acid on the water bath and represented the reaction thus



But Remsen and Lum² showed that it was not the acid that was formed, but it was the acid ammonium salt



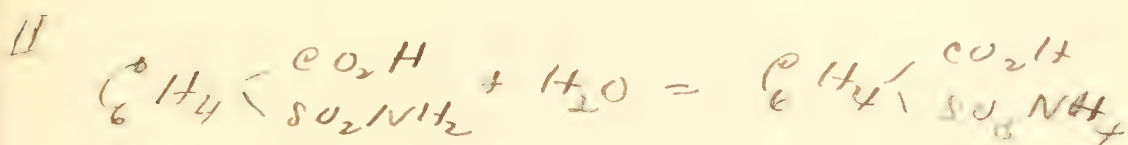
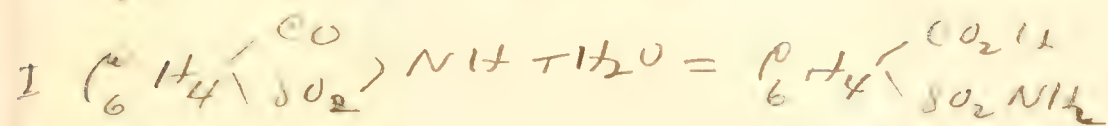
Later Remsen³ and Burton showed that the reaction

¹ Amer. Chem. J. IX 405

² " " " XI 73

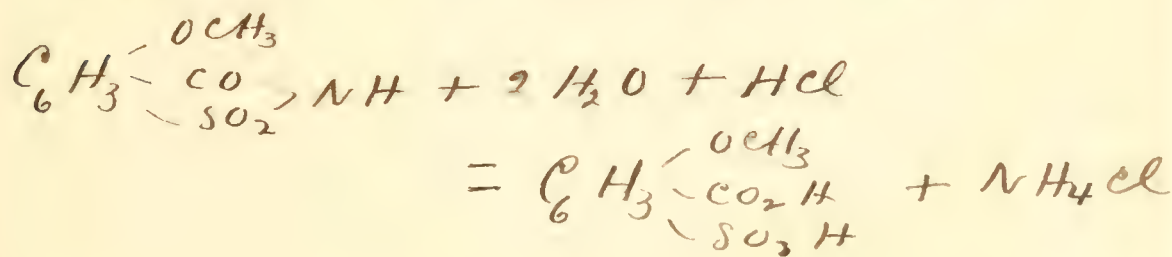
³ " " " XI 403

^{5.11}
~~took~~ place in two stages and
 represented it thus:

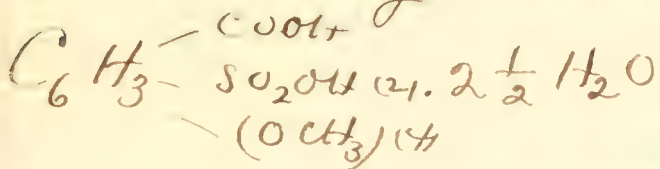


In this case, the conversion of para-methoxybenzoic-sulphonide with hydrochloric acid, the free para-methoxy-ortho-sulpho-benzoic acid was obtained and ammonium chloride isolated.

The reaction can therefore be represented by an equation similar to that given by Brackett and Hayer



Para-methoxy-ortho-sulphobenzoic acid



This acid was prepared according to the method just described - from para-methoxybenzoic-sulphide by boiling out eight ^{parts} of water to one part of concentrated hydrochloric acid by weight. It was also prepared from its acid potassium salt which is formed along with the para-methoxybenzoic-sulphide when para-methoxy-ortho-toluenesulphonamide is oxidized with potassiumpermanganate.

The acid potassium salt is converted into its acid chloride $\text{C}_6\text{H}_3 \begin{array}{l} \text{COCl} \\ \text{SO}_2\text{Cl} \end{array} \text{---} (\text{OCH}_3) \text{---}$ by phosphorus pentachloride and this by boiling with water

into para-methoxy-ortho-sulpho-benzoin acid. It is very soluble in water from which it crystallizes in long needles transparent and colorless.

It melts at 104° and, on cooling, quickly solidifies and melts again at the same point on heating. This may be repeated without change in the melting-point.

Analysis gave the following results.

I 0.1698 grams of substance gave 0.0619 grams of H_2O and 0.2165 grams of CO_2

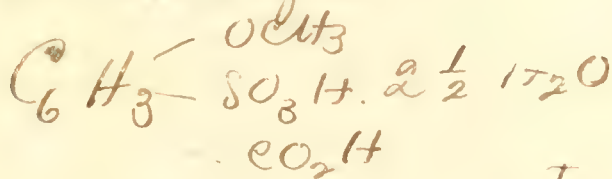
II 0.1758 grams of substance gave 0.0675 grams of H_2O and 0.2238 grams CO_2

III 0.1691 grams of substance gave 0.1494 grams of $BaSO_4$ (Liebig's method)

IV 0.1633 grams of substance gave

0.1408 grams of BaSO_4 (Liebig's method)

Calculated for



			Found.			
			I	II	III	IV
C	34.66		34.77	34.71		
H	4.69		4.05	4.27		
S	11.72				12.14	11.84

The method of combustion used in these analyses and of the sulphoxyl-fluoresceins is that of de Roode.

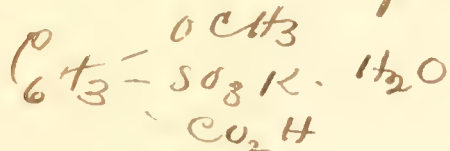
Salts of para-methoxyortho-sulpho-benzoic acid



This salt was obtained in the course of preparation of the paramethoxy-ortho-sulpho-benzoic acid, in several ways as described in the first part of this work. It is very soluble in water, less so in alcohol.

Analysis gave the following results
 0.2659 grams of salt lost 0.0169 grams of H_2O and gave 0.081 grams K_2SO_4

Calculated for



H₂O

6.25

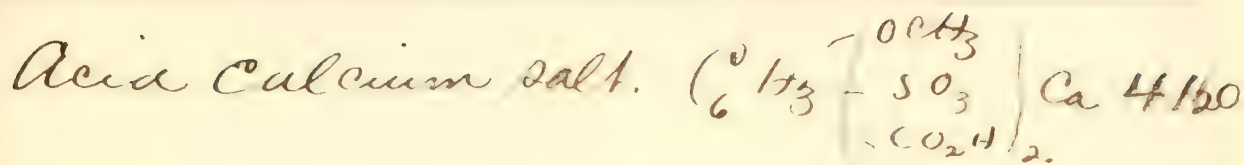
Found

6.28

K

13.58

13.52

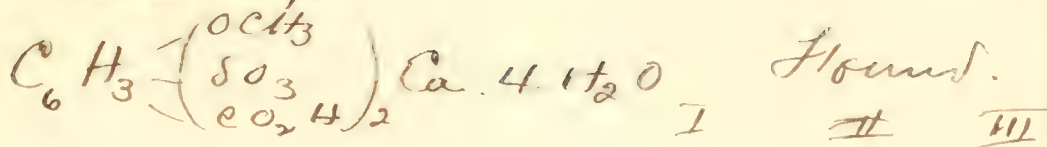


Prepared from the free paramethoxy-ortho-sulphobenzoic acid. A water solution of the acid was divided into two equal parts, one part was neutralized exactly with powdered calcite. To this neutral calcium salt the second part of the acid was added, it was then filtered and allowed to crystallize. It is extremely soluble in water.

Very slow evaporation is necessary to produce good crystals and the specimen of the salt analysed stood over a month before any good crystals separated out that were suitable for analysis.

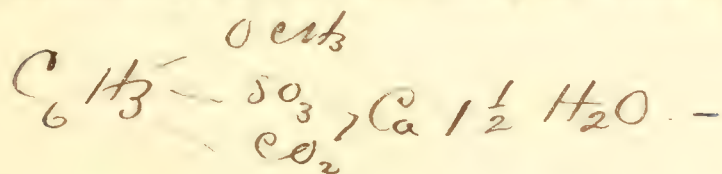
Analyses gave the following

Calculated for



H_2O	12.54	12.66	12.41
Ca	6.15		6.17

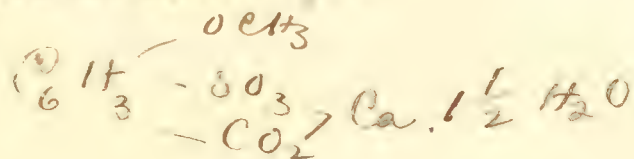
Neutral calcium salt.



Prepared from the free acid by complete neutralization with powdered Calcite. It is extremely soluble in water and could not be obtained in good crystals. After filtering and evaporation almost a dry mass

fine crystal plates separated out.
Analysis gave the following
results:

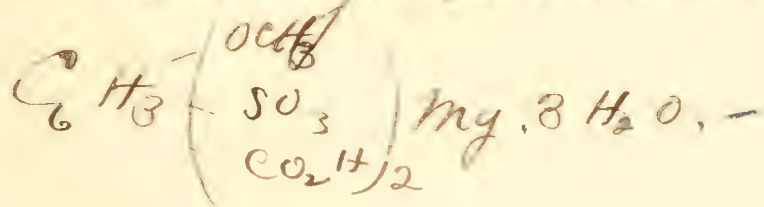
Calculated for.



Found.

H ₂ O	9.09	8.81
Ca	13.46	13.23.

Acid magnesium salt,



This salt was prepared in a similar
manner to the preparation of the
acid calcium salt. It was

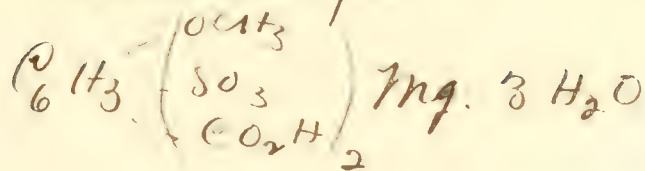
solution of the acid was divided into two equal parts; one part was carefully neutralized with pure magnesium carbonate. To this was then added the other half of the acid solution, forming thereby the acid magnesium salt. It is very soluble in water, but after careful evaporation fine white needles were obtained which proved to be quite efflorescent.

analysis gave the following

I 0.0896 grams of the salt lost 0.0091 grams of H_2O and gave 0.0126 grams of $MgSO_4$

II 0.056 grams of salt gave 0.0025 grams of $MgSO_4$

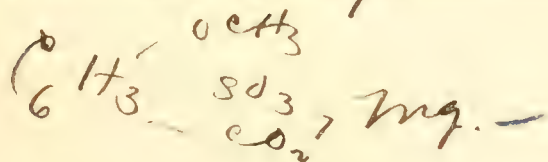
Calculated for



Found.

		I	II
H ₂ O	10.00	10.15	—
Mg	4.44	3.93	4.46

Neutral magnesium salt, —



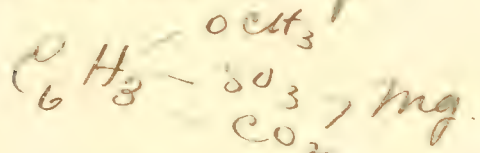
This salt was made from the free acid by exact neutralization with pure magnesium carbonate.

It was found impossible to obtain crystals as the salt was so extremely soluble. The solution was evaporated to dryness and analysed

28

The salt was difficult to get in any quantity good enough for analysis. Analysis gave the following

Calculated for



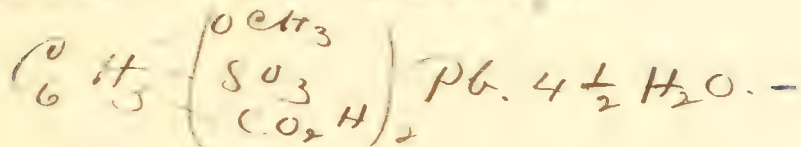
Found

mg.

4.45

4.66

Acid lead salt —

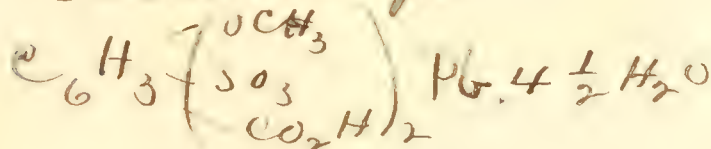


This salt was prepared from the free acid. A water solution of the acid ~~was~~ divided into two equal parts. One part was then neutralized exactly with pure lead

carbonate. To this is then added the other half of the acid solution thus forming the acid lead salt. The solution was filtered and evaporated to a very small volume, when on cooling the salt crystallized out in fine white needles. It is very soluble in water. The salt is volatile at 130° - 140° . It is insoluble in alcohol and petroleum ether.

analysis gave the following
 0.0708 grams of salt at 100° lost
 0.075 grams of H_2O and gave 0.5288
 grams of $PbSO_4$.

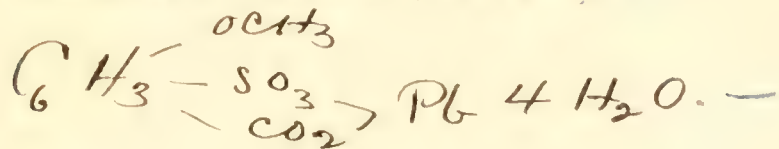
Calculated for



Found

H_2O	10.8	10.59
Pb.	27.60	27.79

Neutral lead salt, —



This salt was made from the free acid. A water solution of the acid was neutralized exactly with pure lead carbonate.

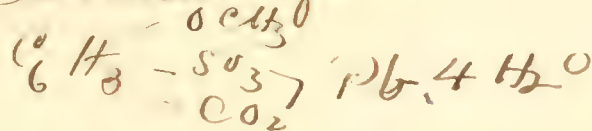
Filtering and evaporation to a very small volume, short fine white needles were obtained.

Analysis gave the following:

I 0.0667 grams of salt gave 0.0395 grams of PbSO_4

II 0.0516 grams of salt lost 0.0073 grams of H_2O at 115° and gave 0.0304 grams of PbSO_4

Calculation for



		Found	
		I	II
H_2O	14.14	—	14.15
Pb.	40.66	40.46	40.25

The extreme solubility of these salts rendered them very difficult to make use of to obtain them in pure condition. The small amounts of salts used for analysis was caused by the lack of sufficient quantity of para-methoxy-ortho-sulpho-benzoic acid.

An attempt to obtain an anhydride

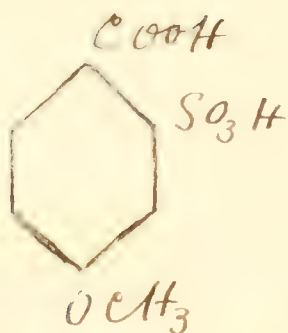
About two to three grams of para-methoxy-ortho-sulpho-benzoic acid were placed in a test tube and gradually heated gently over a free flame and in a sulphuric

acid bath at 100° it lost its water of crystallization and at 104° melted. On heating to 145° it again lost water which condensed on the walls of the tube and crystals sublimed on the upper part of the vessel. They were fine needles. It was found impossible to get possession of them in sufficient quantity for analysis. Upon higher heating the compound broke down yielding decomposition products which had a "fearful" odor nauseating in character.

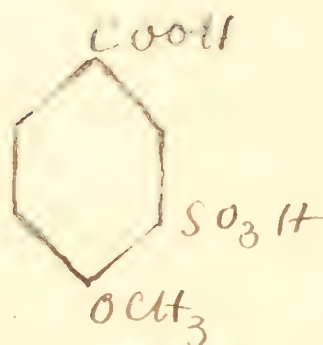
This acid is isomeric with the sulphamic acid of Zervas¹ which has the sulphonic acid group in the meta position to the carboxyl.

¹ Ann Chem. 103 338

The two acids can be represented thus.



Para-methyl-sulpho-benzoic acid



Sulphametic acid of Ferri.

Para-methoxy-sulphon-fluorescein

The first experiment was to introduce two molecules of resorcin into the para-methoxy-ortho-sulpho benzoic acid. Both the resorcin and the acid were carefully dehydrated and then heated together in molecular proportions one molecule of acid to two molecules of resorcin. The method of procedure was as follows. The correctly calculated amounts of the dehydrated acid and resorcin were placed together in a small beaker which was placed in a sulphuric-acid bath. Suspended from above a thermometer was hung reaching into the mixture and which could also be used.

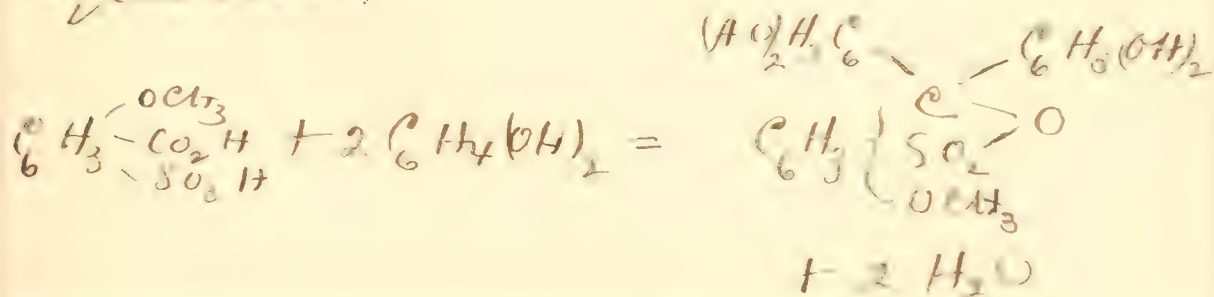
as a stirring-rod. Heat was applied very gently and slowly to the bath. At 65° the resin began to melt and gradually melted till 75° was reached, the mixture becoming a wine-red in color. A few crystals of resin sublimed into the upper part of the beaker. The heat was gradually raised till 110° - 115° was reached and the thermometer kept at that temperature as long as the reaction would permit. The reaction went smoothly at that temperature. Stirring must be kept up all the time, as it is necessary for the reaction otherwise it appears not to take place. When it is stirred the temperature rises and the heat is removed.

This same use of temperature, and necessity of stirring was noticed by Blackshear. After heating two hours the mass became viscous and reddish black in color. It became solid on slight lowering of the temperature, and in some cases it was necessary to raise the temperature in order to keep the mass liquid in order to be able to stir it. On cooling, the fused mass solidified and the surface was glossy with a resinous lustre. The cooled mass was then treated with water to dissolve out any unacted upon resorcin or acid, and other soluble matter. The fused mass was then dissolved in sodium hydrate, in which

about it is soluble, and then precipitated with hydrochloric acid, when the sulphone-fluorescein comes down as a reddish, granular precipitate. This was washed thoroughly with hot and cold water by decantation. It is then placed on a filter and by the aid of a filter-pump washed again. The washing of the sulphone-fluorescein is very important.

In drying the sulphone-fluorescein great difficulties were encountered. When dried on a drying-plate it lost water as was shown by analysis. Next, drying over sulphuric acid was tried and in this case also the sulphone-fluorescein lost water.

The best method for drying it was found to be to dry it as thoroughly as possible by the aid of the filter-pump; allow it to stand over night; and then dry it between sheets of drying-paper. It then appears as a brown-red amorphous mass which is finely ground for analysis. In this manner from one to two grams of the dehydrated acid and the requisite quantity of dehydrated resorcin for two molecules was used. The reaction taking place according to this equation:



The substance was very difficult to burn and the analytical results indicate that an impure sulfon-fluorene of the formula above given was formed. Different specimens and the same specimen were analyzed several times but no constant results could be obtained. Analysis gave the following

0.0802 grams of the substance gave 0.1688 grams of CO_2 and 0.0384 grams of H_2O

	Calculated for $\text{C}_{20}\text{H}_{16}\text{O}_8\text{S}$	Found
C	57.69	57.15
H	3.87	5.31

in other analysis gave C 59.3% and H 5.49%.

An analysis for sulphur gave

S^P 6.44% while the calculated percentage for the above formula is 7.37%. (Some of the Ba SO₄ went through the filter which accounts for the low figure obtained.)

The sulpho fluorescein is insoluble in all ordinary solvents. Soluble in caustic alkali with a beautiful red green fluorescence.

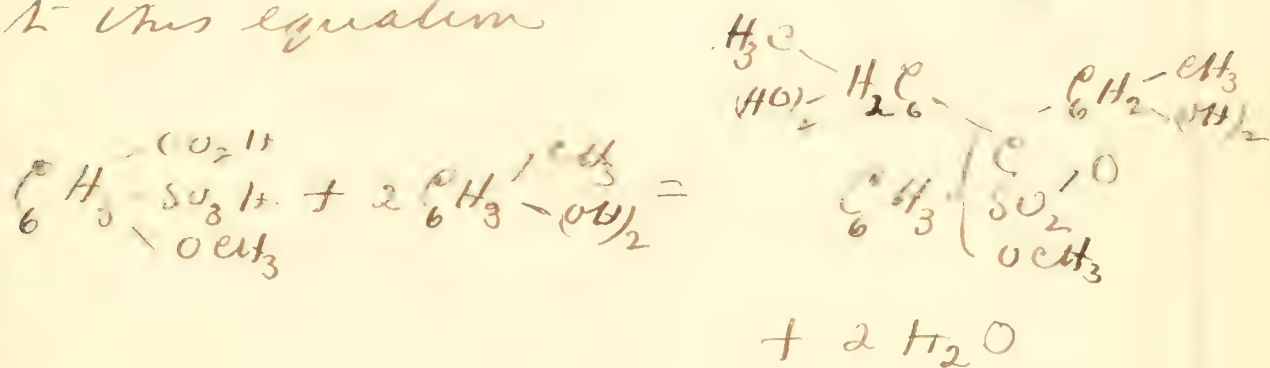
Precipitated from its alkaline solution as a red granular precipitate by hydrochloric acid.

Preparation of the Orcin Compound

Orcin was substituted for resorcin in ^{the} hopes of getting a purer product.

The method of procedure was the same as in case of the resorcin using one molecule of acid to two molecules of orcin, both being carefully dehydrated. The orcin melted at 65° to 75° and reaction began at 110° water being given off. The temperature in this case had to be raised to 145° in order to complete reaction, stirring being kept up all the time. The manner of washing, filtering, dissolving, precipitation and drying was the same as in case of the resorcin compound.

The yield was about 50%. The reaction takes place according to this equation



The main product is a better substance to deal with than the sulphonic fluorescein obtained with resorcin.

The same difficulties in drying were also encountered here.

In alkaline solution it gives a similar fluorescence and is precipitated as a red granular precipitate by hydrochloric acid from its alkaline solution.

Analysis

An analysis was made to see if there was water in the compound. The substance was heated at $110-115^{\circ}$ with loss of water and on raising the temperature no more water was given off. Analyses gave the following

I 0.0578 grams of substance at $110-115^{\circ}$ lost 0.0024 grams of H_2O

II 0.0529 grams of substance gave 0.0271 grams of H_2O and 0.1140 grams of CO_2

III 0.0602 grams of substance gave 0.0312 grams of H_2O and 0.1304 grams of CO_2

IV 0.1076 grams of substance gave 0.0512 grams of $BaSO_4$ (Liebig method)

V 0.1330 grams of substance gave

0.5634 grams Ba SO_4 (Liebig method)

Calculated for					Found				
$\text{C}_{22}\text{H}_{20}\text{O}_8\text{S}_7\text{H}_2\text{O}$					I	II	III	IV	V
H_2O	3.39				4.15				
C	57.14				58.76	59.07			
H	4.76				5.69	5.75			
S	6.92							6.63	6.84

These analyses show that undoubtedly a sulphur fluorescein of the above formula was ^{partially} formed, but that it was not pure. It was found impossible to purify it.

Blackman also found it impossible to purify the sulphur fluorescein formed from ortho-sulpho-benzoic acid and resorcin according to the above method. He prepared it

from di-*o*-*o*-benzoyl benzene sulphonic acid.

Action of Phenol.

in attempt to introduce two residues of phenol into the para-methoxy-ortho-sulphobenzonic acid was tried. The method of procedure was the same as followed in the case of resorcin and orcin.

The phenol began to melt at 45° and was all melted at 65° .

Slight action began at 85° and at 105° ; on stirring, the thermometer rapidly rose to 130° , indicating reaction, the liquid becoming wine-red in color. The temperature was kept at 115° - 120° as nearly as possible, then the temperature

was raised to 124° . By continuous stirring the substance gradually became stiff. On cooling it was treated in the same manner as in case of the resorcin and-
 orcin compounds. Precipitated from its solution in sodium hydroxide by hydrochloric acid it is a dirty brown mass with which it was found impossible to deal.

Summary

That para-methoxy-ortho-toluene-sulphonicamide is oxidized by potassium permanganate to para-methoxy-benzoin-sulphonic acid and that the presence of a small

quantity of caustic alkali materially helps the oxidation.

That para-methoxy-benzoin-sulphonic when boiled with water and hydrochloric acid passes over directly into the free para-methoxy ortho-sulpho-benzoic acid, and no acid ammonium salt could be found. ^{According to this, the} These look like the presence of the methoxy group ^{causes} ~~influences~~ the formation of the free acid.

That it is very difficult to obtain a pure sulphonic fluorescein by treatment of the free para-methoxy ortho-sulpho-benzoic acid with resorcin or orcin and the

78
purification of the same offers
considerable difficulty. A better
method would be like that used
by Blackshear who prepared
the sample sulphur fluorescein
from di-*ortho*-benzoyl-benzene-sulphonic
acid

87
The Action of Absolute Methyl
Alcohol on Para- meta- Ortho
Toluene - Sulphonic Acid in
the Presence of certain Substances

Decomposition of Para-diazoothotoluene
sulphonic acid with Methyl Alcohol
(absolute) in the presence of certain
substances.

Introduction

Bleson¹ found that when diazo-
benzene sulphate or nitrate were
decomposed with sodium methylate
or ethylate, ~~that~~ the hydrogen
reaction took place. Dushell²
working on the decomposition of
para-diazoothotoluene sulphonic acid
under different conditions of tempera-
ture and pressure found in case
of ethyl alcohol (absolute) that both
reactions took place and that
high pressure favors the ethoxy
reaction and low pressure the

¹ Amer Chem. J. XVI 235-

² " " " XV 105-

the hydrogen reaction. Also that the decomposition itself is a function of temperature as well as of pressure, but left open the question as to what influenced the course of the reaction the more. Park's also working on the decomposition of the above diazo compound with methyl alcohol (absolute) found that the methoxy product only was formed at ordinary, increased, or diminished pressure, namely para-methoxy-ortho-toluene sulphonic acid. At the suggestion of Prof. Ransom the decomposition of the above diazo compound with sodium methylate and ethylate was undertaken in the presence of absolute methyl and ethyl alcohols. Also the decomposition with absolute

methy. alcohol in the presence of ammonia, substituted ammonias and potassium hydrate.

Preparation of the Diazo Compound.

The diazo compound was prepared according to the method used by Dashiell¹ and Parks² and followed by me in the first part of this work.

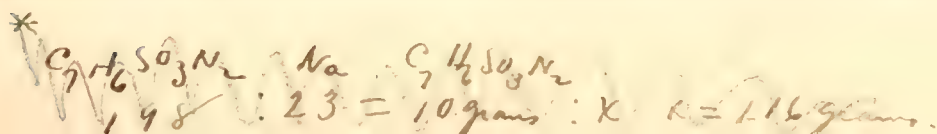
Decomposition in presence of Sodium Methylate

The sodium methylate was made by dissolving in a definite

¹ Amer. Chem. J. XV 105

² " " " XV 320

volume of absolute methyl alcohol
 a known weight of sodium forming
 sodium methylate. Knowing the
 strength of the sodium methylate
 the amount necessary for complete
 reaction with the diazo compound
 can be readily calculated. ~~The~~ ^{the} ~~is the~~
~~required~~ * amount of sodium methylate
 for ten grams of the diazo compound
~~was calculated out and poured into a~~
~~beaker.~~ To this was added some
 absolute methyl alcohol. The
 diazo compound was added gradually
 to the sodium methylate solution.
 Evolution of nitrogen took place.
 The temperature was kept down to
 about 20° during the reaction by a
 cooling mixture as the temperature
 rises rapidly on addition of the



diazo compound. After the calculated
 amount of diazo compound had
 been added and nitrogen had
 ceased to come off, the liquid
 was evaporated to dryness on the
 water bath. It was then finely
 powdered and treated with a
 slight excess of phosphorus
 pentachloride, to pass ^{the} the
 chloride. The chloride was washed
 and then treated with concentrated
 ammonia to pass ^{convert it into} the amide
 of orthotoluene-sulphonic acid

$$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ | \\ \text{SO}_2\text{NH}_2 \end{smallmatrix}$$
 if the hydrogen-
 reaction had taken place
 in the decomposition of the diazo
 compound. The amide was formed.
 It was crystallized from water ^{and was obtained} coming
 down in fine white needles

It melted at 154° which is the melting point of ethotoluenesulfonamide. This shows that the hydrogen reaction did take place to some extent. The yield is small but the reaction is very interesting in that it shows that the presence of the alkali tends to cause the hydrogen reaction to take place to some extent, following in the line of Beeson's observations, while Parks found that with the absolute methyl alcohol alone only the methoxy product was formed. The residue left was a black larry mass with which nothing satisfactory could be done.

Decomposition with Sodium Ethylate

The sodium ethylate was made in a similar manner to the sodium methylate using absolute ethyl alcohol. As before ten grams of the diazocompound were used, and the method of decomposition ~~was~~ ^{was} the same as in case of the sodium methylate. The action was the same as in case of the sodium methylate though less vigorous. When placed in ice-water the reaction in the beaker stopped. Aldehyde was formed, ~~detected~~ ^{indicated} by its odor. On filtering, a considerable residue was left on the filter. It was a larry mass from which nothing satisfactory could be obtained.

The filtrate was evaporated to dryness. Neither from the residue nor filtrate could ortho-toluenesulphonamide be obtained. Both the residue and filtrate are reddish black lustrous substances and extremely difficult to work with.

Decomposition of the Diazo Compound with absolute Ethyl Alcohol in the presence of Potassium hydroxide.

In this experiment nothing pure was obtained. The action was less vigorous than that of the decomposition with sodium methylate or ethylate. The method of procedure of the decomposition

was the same as before. After the
ten pairs of leaves compound had
been added to the calculated
weight of potassium hydrate in
a sufficient quantity of absolute
ethyl alcohol, to insure complete
decomposition, the contents of the
beaker were transferred to a pressure
flask and gently heated. Some
decomposition took place at 700^{mm}
pressure. In about an hour the
alcohol boiled gently, all gas
having stopped coming off. The
solution was dark red. On filtering
a black carbonaceous mass was
left on the filter. From the filtrate,
by evaporation and drying, a red solid
mass was obtained which turned
to a black gummy mass in the air.

Analyses of sulphur and potassium
showed that the products were
sulphides. It was found impossible
to get a pure product

Decomposition of the diazo compound
with absolute methyl alcohol saturated
with dry ammonia gas.

To the requisite amount of methyl alcohol
(absolute) saturated with dry ammonia
gas. absolute methyl alcohol was
added. To this was gradually added
ten grams of diazo compound. It
reacted at ordinary temperature,
some slight heating to 30° - 35°
accelerated the reaction. Gas was

ground off. After the reaction was over the liquid was evaporated to dryness in the water-bath.

The substance was finely powdered and ^{by} ~~most~~ ^{increasingly} ~~increasingly~~ treated with excess of phosphorus pentachloride to convert the chloride. After washing the chloride, it was treated with concentrated ^{and} ammonia to convert it ^{to} amide. the formula

The amide was crystallized from water and the melting-point taken. It melted at 164° which is the melting point of the amide of parabromidine. orthosulphonic acid from which acid the diazo compound had been made. For further confirmation the dried product was treated with concentrated hydrochloric acid to convert it free acid

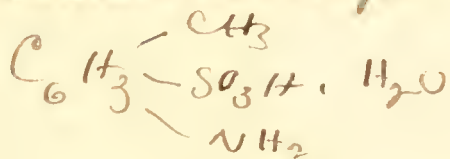
The solution was evaporated down on the water-bath and then allowed to crystallize. Filtered off and washed well. The acid is insoluble in cold water, difficultly soluble in boiling water. Recrystallized from boiling water it comes down in glittering rhombohedral plates.

Analysis gave the following--

1 0.0834 grams of substance gave 0.0984 grams BaSO_4 (Liebig method)

4 0.1106 grams of substance gave 0.1240 grams BaSO_4 (Liebig method)

Calculated for



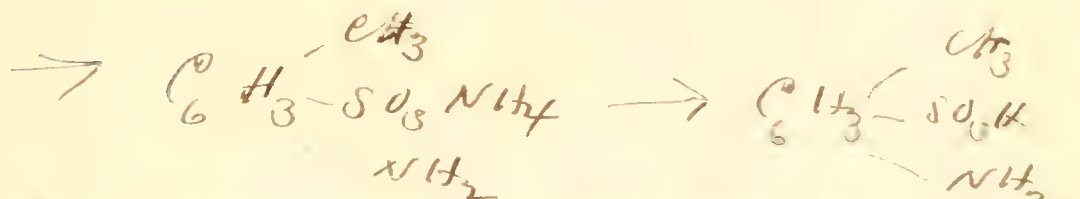
Found

I II

S	15.61	15.72	16.02
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A similar reaction has been

shown to take place by Mr Griffin working in this laboratory in case of the diazo compound of para-toluidine-meta-sulphonic acid with absolute methyl alcohol saturated with dry ammonia gas. The course of the transformation is expressed thus



The specimen of the diazo compound used, was tested for any undiazotised para-toluidine-ortho-sulphonic acid and no undiazotised acid was found.

Decomposition with absolute
Methyl Alcohol and Aniline

Having shown that para-diagno-
ortho-toluene sulphonic acid was
converted back to the para toluene
ortho sulphonic acid by
absolute methyl alcohol and
ammonia, it was thought to try the
~~use of~~ substituted ammonias, ^{the action}
and aniline was used. As before,
each specimen of diazo compound
was tested for any undiazotised
acid. In no case was any appre-
ciable quantity of free acid found.
In this case three reactions take
place according to the proportions
of aniline and methyl alcohol
used, yielding one common

product and what appears to be three or four different dye-stuffs. A fourth reaction takes place on gentle heating with no evolution of gas and yielding a dye-stuff.

Case I

In this case one volume of aniline to two volumes of absolute methyl alcohol were used. Generally 30^{cc} of absolute methyl alcohol to 15^{cc} of aniline. The mixture of aniline and methyl alcohol was poured into a beaker and gently heated. When the alcohol was almost boiling the diazo compound was added in small quantities. There was a strong

evolution of nitrogen, the color
changed to a deep red, and
after a time the solution became
viscid. The diazo compound was
added ^{with} till the evolution of nitro-
gen ceased it was exceedingly weak.
The mass was transferred to an
evaporating dish and very methyl
alcohol evaporated off. The
black tarrey mass left in the
dish was boiled out water and
filtered. On cooling the filtrate
clouded up to a red color and
crystals of a beautiful golden
color separated out in scales.
The black dried mass after
several such treatments with water
became brittle, and the golden
scales could be seen in it.

The golden scales (A) were filtered
off and dried between sheets of
drying paper. The yield is good.
The filtrate from the scales was
evaporated down, and a mass
of black rhombohedral crystals
separated out. These were purified
with animal charcoal, crystallizing
out in beautiful rhombohedral
plates and crystals. The yield
is good. Analysis gives the
following

I 0.1132 grams of substance gave
0.1810 grams of BaSO₄

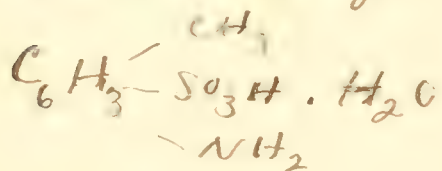
II 0.1665 grams of substance gave
0.1434 grams of BaSO₄

III 0.1338 grams of substance gave
7.52^{cc} (corrected) of N.

IV 0.2830 grams of substance gave

15.95° correction of N

Calculated for



		I	Found II	III	IV
S	15.61	5.89	15.87		
N	6.78			7.05	7.07

These analyses and the other properties of the substance showed that the product was para-toluidine-ortho-sulphonic acid and that aniline had played the same part as ammonia had done in the other experiments, causing the reformation of the original acid, para-toluidine-ortho-sulphonic acid. For the further testing of the product the following experiment was done. Upon the basis of the analyses that the product was para-toluidine-ortho-sulphonic acid then it could be

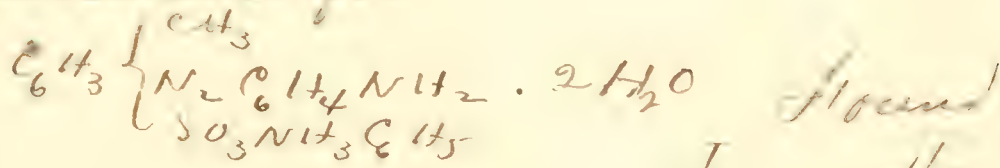
converted into para-methoxyortho-toluene-sulphonamide and be identified by its melting point. The directions for its above conversion as given by Parks were followed. The conversion was easily accomplished, and a sulphonamide melting at 151° was obtained which identified it as para-methoxyortho-toluene-sulphonamide. Thus the evidence was conclusive as the sulphonamide is formed from paratoluidine-ortho-sulphonic acid in the way given, therefore the substance must have been paratoluidine-ortho-sulphonic acid with which we started.

Analysis for nitrogen in the golden scales A were as follows

1. 0.21488 grams of substance gave 12.61% of N.

II 0.22683 grams of substance gave 12.16%
of N.

Calculated for



N	12.86	12.61	12.76
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These analyses are only preliminary
and are suggestions only.

1 These analyses were kindly made by Mr.
E.W. Magnus of this laboratory who used Raiffle's
modification, plus Will-Vanvankop method for Nitrogen

7
A comparison with absolute methyl
alcohol and Aniline with a greater
amount of methyl Alcohol.

11

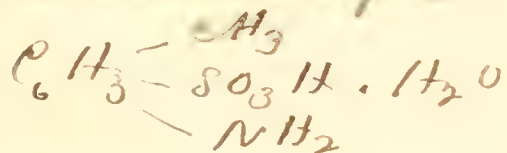
In this case one volume of aniline
to five volumes of absolute methyl
alcohol were used. The experiment
was conducted in the same manner
as given under Case I. There was
strong evolution of nitrogen, the
color of the solution changing from
red to dark brown. The solution
after the reaction was over was filtered
leaving a dark precipitate on the
filter. This precipitate was purified
as much as possible with acetone
which removed a great deal of the
color and leaves when dried a
reddish brown powder. The powder

was treated with hydrochloric acid and then boiled with animal charcoal when on filtering the glistening rhombohedral plates of para toluidine ortho sulphonic acid came down. By slow crystallization large rhombohedral crystals were obtained. Analysis was as follows.

I 0.2315 grams of substance gave 0.2771 grams BaSO_4 (Liebig method)

II 0.1885 grams of substance gave 7.13/8 N. (absolute method)

Calculated for



Found

S 15.61 16.03

N 6.78 7.13

The residue obtained by evaporation of the filtrate from the red powder

was not investigated through lack of time, but this work will be continued later.

Decomposition with Aniline two volumes and Methyl alcohol absolute one volume.

III

In this case generally 30 cc of aniline to 15 cc of absolute methyl alcohol were used. The mixture of aniline and alcohol was heated to boiling. The diazo compound was gradually added stirring all the time. The diazo compound was added ^{gradually} ~~all~~ and all the gas was given off. The color changed from a dark red to brown, when the operation

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was finished, the solution became
stiff and had the appearance of a
tar. It was then evaporated to
dryness in a water bath. To the
mass thus formed water ^{was} added
and the mixture boiled. It was
then filtered. The filtrate became
cloudy and golden scales (B)
crystallized out. From the filtrate
from these golden scales by
evaporation, purification by
boiling with animal charcoal, and
crystallization the original
para-toluidine-ortho-sulphonic-
acid was obtained. Also
the black tarrey mass was
treated with a small quantity
of concentrated hydrochloric
acid. The addition of the acid

turned the color to a reddish purple, and sometimes purple scales were formed, and sometimes an amorphous red precipitate when water was added. It was then boiled with water and filtered. The filtrate becomes cloudy and from a deep red solution feathery reddish needles crystallized out (C). On recrystallization of the needles the solution becomes more yellow in color. From the filtrate of the red needles (C) by evaporation, purification, with animal charcoal, and crystallization the original para-toluidine-ortho-sulphonic acid was obtained. From some preliminary work on the dye stuff it is probable that the red needles (C)

contain about 21.5% of nitrogen.
 Analyses of the red needles were as follows

I. 1.001 grams of substance gave 17.06 cc of N
 equal to 21.42% of N. (absolute method)

II 0.0623 grams of substance gave 12.1 cc of N.
 equal to 21.68% of N. (absolute method)

III 0.1375 grams of substance gave 0.033 grams BaSO_4
 equal to 3.30% of S. (Carius method)

IV 0.1250 grams of substance gave 0.0287 grams
 of BaSO_4 equal to 3.16% of S. (Carius method)

A preliminary determination of nitrogen and sulphur in the golden scales (B) give about 14.4% of N and 8.3% of S.

The work on all the ^{compounds} dye-stuffs here mentioned is still in progress, and no definite statement is wished to be made until further

1 analyses I, III & IV were kindly made by Mr. G. W. Gray of this laboratory

work has been done upon them. Such remarks ~~that~~^{as} have been made are suggestions only. The analyses are only preliminary. Work of the same nature, as above, with sulphamic acid is in progress in this laboratory, and appears to ~~fasten~~^{compare} with that recorded. Give similar results.

Summary

In conclusion, it appears that the presence of sodium methylate causes the hydrogen reaction to take place to some extent in the decomposition of para-diortho-toluene sulphonic acid with absolute methyl alcohol. That the reaction takes place at ordinary room temperature

ature and at ordinary pressure.

2. That the decomposition of para-diaz-ortho-toluene-sulphonic acid with absolute methyl alcohol, saturated or partly saturated with dry ammonia gas, causes the ammonium salt of para-toluidine-ortho-sulphonic acid to be formed, to which salt breaks down as treated for the original para-toluidine-ortho-sulphonic acid, the acid from which the diazo compound was made.

3. That the decomposition of para-diaz-ortho-toluene-sulphonic acid with absolute methyl alcohol and aniline, in different proportions by volume, causes the reformation of the original acid para-toluidine-ortho-sulphonic acid and certain ^{other products} ~~stuff~~ ^{that have not as yet been ~~fully~~ studied.}

Biographical Sketch

The author of this dissertation, Philip Randle Moale, the eldest child of J. Gorkham Moale, was born January 21st 1867 at Baltimore Maryland. He was educated in the public and private schools of Baltimore and at the Baltimore City College. He entered Johns Hopkins University October 1886 and received the degree of Bachelor of Arts in June 1889, having followed what is known as Group IV in the Collegiate department of the university, Chemistry and Physics being the principal subjects. The next five years were spent in graduate work in this university with Chemistry as the principal subject.



mineralogy and geology as the
two subordinates. In 1891 he
was appointed ^{lecturer} assistant to
Professor Renssler, which position
he filled for two years.



3 1151 00565 0886

FRAGILE
DOES NOT
CIRCULATE

